Time Dependent Effects and Transport Evidence for Phase Separation in $La_{0.5}Ca_{0.5}MnO_3$

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Abstract

The ground state of $La_{1-x}Ca_xMnO_3$ changes from a ferromagnetic metallic to an antiferromagnetic charge-ordered state as a function of Ca concentration at x $\sim$ 0.50. We present evidence from transport measurements on a sample with x = 0.50 that the two phases can coexist, in agreement with other observations of phase separation in these materials. We also observe that, by applying and then removing a magnetic field to the mainly charge-ordered state at some temperatures, we can "magnetically anneal" the charge order, resulting in a higher zero-field resistivity. We also observe logarithmic time dependence in both resistivity and magnetization after a field sweep at low temperatures.

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Among all the colossal magnetoresistance manganites [1–4] $La_{1-x}Ca_xMnO_3$ is particularly interesting. It can be prepared over the whole range of doping (x) ($0 \lesssim x \lesssim 1$), and thus provides an insight into the properties of rare-earth manganites as a function of doping. The ground state of this compound ranges from a ferromagnetic metallic (FMM) at low doping ($0.2 \lesssim x \lesssim 0.45$) to an antiferromagnetic (AFM) charge-ordered (CO) state at high doping $x \gtrsim 0.50$. The concentration regime at $x \sim 0.50$ [5–8] is particularly interesting since in this regime the FM metallic state becomes unstable to an insulating charge-ordered state. However, recent magnetometry and neutron studies have detected a weak FM moment of a few fraction of Bohr magneton/ion even in the charge-ordered regime. This can be explained by a homogeneous model, e.g., a canted AFM state or by a phase-separation into inhomogeneous state, although recent theoretical and experimental studies on this characteristic have shown overwhelming evidence for phase separation in this and other doped manganites [5,9–21].

In this paper, we report a study of $La_{0.5}Ca_{0.5}MnO_3$, where the ground state changes from a conducting FM ($x < 0.50$) to a charge-ordered AFM state ($x \gtrsim 0.50$) (additional data are also presented in other publications [21,22]). The resistivity (ρ) was measured by standard ac four probe in-line method with the magnetic field perpendicular to the direction of the current, magnetization (M) with a commercially available SQUID magnetometer, and heat capacity (C) was measured by semi-adiabatic heat-pulse method. The sample was prepared by a standard solid state reaction and the Mn^{4+} content was measured to be 53.8% by redox titration.

Figure 1 shows $\rho(T)$ and M(T) at different fields measured on both warming and cooling. On cooling, M(T) displays a FM transition at T_c, however, at a lower temperature T_{co}, M(T) drops sharply with an accompanying rise in $\rho(T)$ due to the charge-ordering of the Mn^{4+} and Mn^{3+} ions. Both M(T) and $\rho(T)$ exhibit large hysteresis at this transition, indicating the strongly first order nature of the transition. Furthermore T_{co} decreases monotonically with increasing external field, indicating that the CO state becomes energetically less favorable in an external field [21]. The resistivity, $\rho(T)$, shows only activated behavior in low fields, but

for H $\gtrsim$ 3 T, at temperatures well below T_{co}, $\rho(T)$ reaches a maximum before subsequently dropping at lower temperatures (see inset to 1). The temperature of the maximum in $\rho(T)$ increases with increasing field, leading to an enormous magnetoresistance [10] which has been referred to as the "melting" of the charge ordered state. The existence of a maximum and subsequent decrease in $\rho(T)$ can be attributed to the presence of free carriers in the charge ordered state, and the large low temperature magnetoresistance can be attributed to an increase in the population of the free carriers. The solid line in the inset is a fit to the data assuming the coexistence of free carriers and charge order as has been described previously [21]. Fits to the $\rho(T)$ data at different fields indicate that the "melting" proceeds by an increase in the number of free carriers, but that even in a 9 T field only a small fraction of the charge order is dissociated, as is also indicated by a rather large ρ ($\rho \sim 0.1$ Ωcm) at high fields. It should be noted that this sort of coexistence is seen in a range of samples with $0.48 \lesssim x \lesssim 0.55$ in $La_{1-x}Ca_xMnO_3$ and also in other materials including high quality single crystals [23].

To characterize the dissociation of the CO state in an external magnetic field, we studied $\rho(H)$ and M(H) as a function of field as shown in figure 2. Our samples were zero-field cooled to the prescribed temperature and $\rho(H)$ and M(H) were measured as a function of field, when the field was swept from H = 0 $\rightarrow$ H_{max} , H_{max} $\rightarrow$ -H_{max} and -H_{max} $\rightarrow$ H_{max}, where H_{max} was 9 T for the resistivity and 7 T for the magnetization measurements. At low temperatures (T $\lesssim$ 60), $\rho(H)$ drops with increasing field [24]. During subsequent field sweeps, while $\rho(H)$ displays a large hysteresis, M(H) remains largely non-hysteretic at high fields. On decreasing the field $\rho(H)$ increases, but it always remains considerably smaller than during the initial sweep. This perhaps suggests that even though the charge-lattice is not totally dissociated at H $\sim$ 9 T, at the lowest temperatures the delocalized electrons remain primarily dissociated even when the field is removed. At intermediate temperatures (70 $\gtrsim$ T $\gtrsim$ 140), where the conduction is primarily through excitations in the charge lattice, $\rho(H)$ also decreases with increasing field. At lower fields (H $\lesssim$ 1 T), however, $\rho(H)$ rises above the initial sweep, such that $\rho(H = 0)$ is higher than the initial ZFC ρ of the sample.

Similar behaviour was also observed in high quality single crystal samples of $Pr_{0.50}Sr_{0.50}MnO_3$ [25] and $Nd_{0.50}Sr_{0.50}MnO_3$ [22]. We speculate this increase in $\rho(H)$ at low fields is due to field-induced "annealing" of the charge-ordered state, i.e., by sweeping the field up and back, more perfect charge-ordered states with correspondingly higher resistivity are created. At temperatures of the order of T_{co}, this annealing effect disappears but the sample continues to show large magnetoresistance. This is probably also attributable to the enhancement of the ferromagnetic phase in the sample, but at these temperatures the enhancement is apparently reversible since the $\rho(H = 0)$ is recovered after sweeping the field.

The competition between the phase separated AFM CO and FMM states can be expected to lead to interesting time dependent effects of the sort seen in spin glasses (due to the local frustration between AFM and FM exchanges [26]). In particular, since the relative fraction of the phase separated materials can be altered by the application of an external magnetic field, one might expect to observe time dependence in the physical properties which is attributable to the changing phase separation. In order to examine such effects, we measured the resistivity, magnetization and heat capacity of this sample as function of time after changing the magnetic field. In each case, the sample is zero field cooled to the prescribed temperature, the field was raised, and then measurements were performed as a function of time. Both zero field cooled ρ and M relax monotonically as function of time in an external field with a logarithmic time dependence as shown in figure 3, but C which shows a sharp rise in the first 10 minutes after applying a 9 T field remains time-independent afterwards. Furthermore, the time dependence might be more pronounced in transport preoperties than the magnetization since one can imagine that there are parallel conductive paths, which would increase the conductivity of the sample. And we observe that while the magnetization increases by only around 0.5% over a period of 24 hours, ρ decreases by as much as 60% in the same period of time. The time dependence of M and ρ is similar to magnetic viscosity or magnetic after-effects observed in soft irons [27] and spin glasses. Similar time-dependent relaxation in ρ was also observed in $La_{2/3}Ca_{1/3}MnO_{3+\delta}$ [28], and $Pr_{2/3}Ca_{1/3}MnO_3$ [29] which were also observed to display evidence of some glassy

behaviour by recent μ spin resonance [30] and neutron diffraction [31] experiments. Figure 3 shows that at H = 7 T and 9 T respectively, both M and ρ can be fitted to a linear function of logarithm of time, i.e., $M = Slogt + const.$. A preliminary study of the slope (S) as a function of temperature reveals some interesting features, and which are the subject of ongoing investigation.

This research has been supported by NSF grant DMR 97-01548, the Alfred P. Sloan Foundation and the Dept. of Energy, Basic Energy Sciences-Materials Sciences under contract #W-31-109-ENG-38.

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FIGURES

FIG. 1. The top panel shows the resistivity of the sample as a function of temperature on cooling(solid) and warming(open) at H = 0 → 9 T in steps of 1 T. The bottom panel shows the magnetization of the sample as a function of temperature on cooling(solid) and warming(open) at H = 1 T → 7 T in steps of 2 T. The inset illustrates two distinct features in $\rho(T)$ associated with the coexistence of two states. The solid line is fit to the data as discussed in the text.

FIG. 2. The left and the right panels show the resistivity and magnetization of the sample as a function of field at different temperatures. All the measurements were done when the field was swept from 0 → 9 T (open circles), 9 T → -9 T (solid lines) and -9 T → 9 T (dashed line).

FIG. 3. The time dependence of $\rho(t)$ and M(t) at T = 5 K and H = 9 T and 7 T respectively. Both resistivity and magnetization data is fitted with the functional form, $\rho = Slnt + const.$ (solid line). In addition a fit of the form $\rho = Aexp(-BT)$ is also illustrated by dashed lines. The inset shows C(t) at H = 9 T and T = 5.5 K.

Figure 1 M. Roy *et al.*

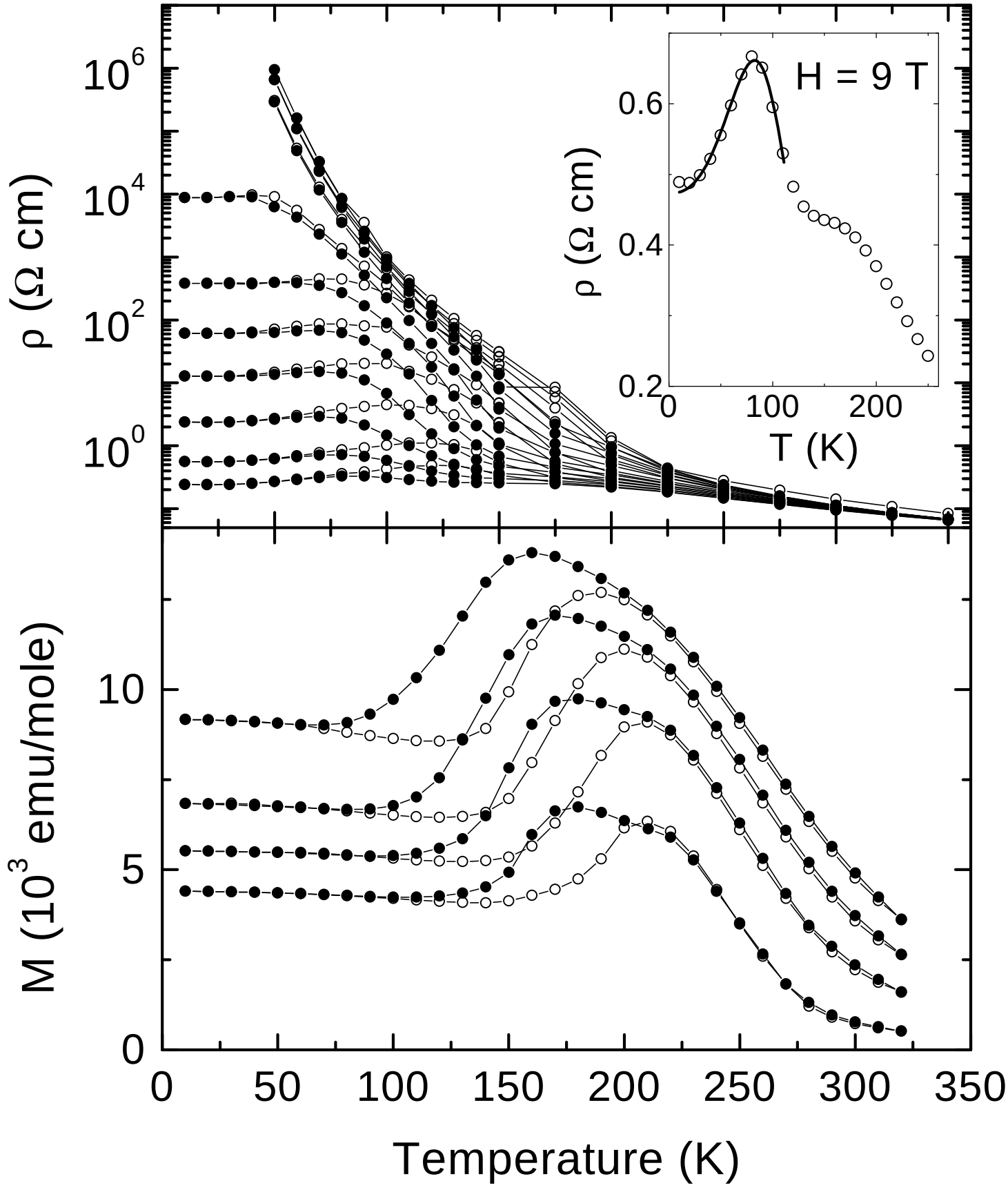

Figure 2 M. Roy *et al.*

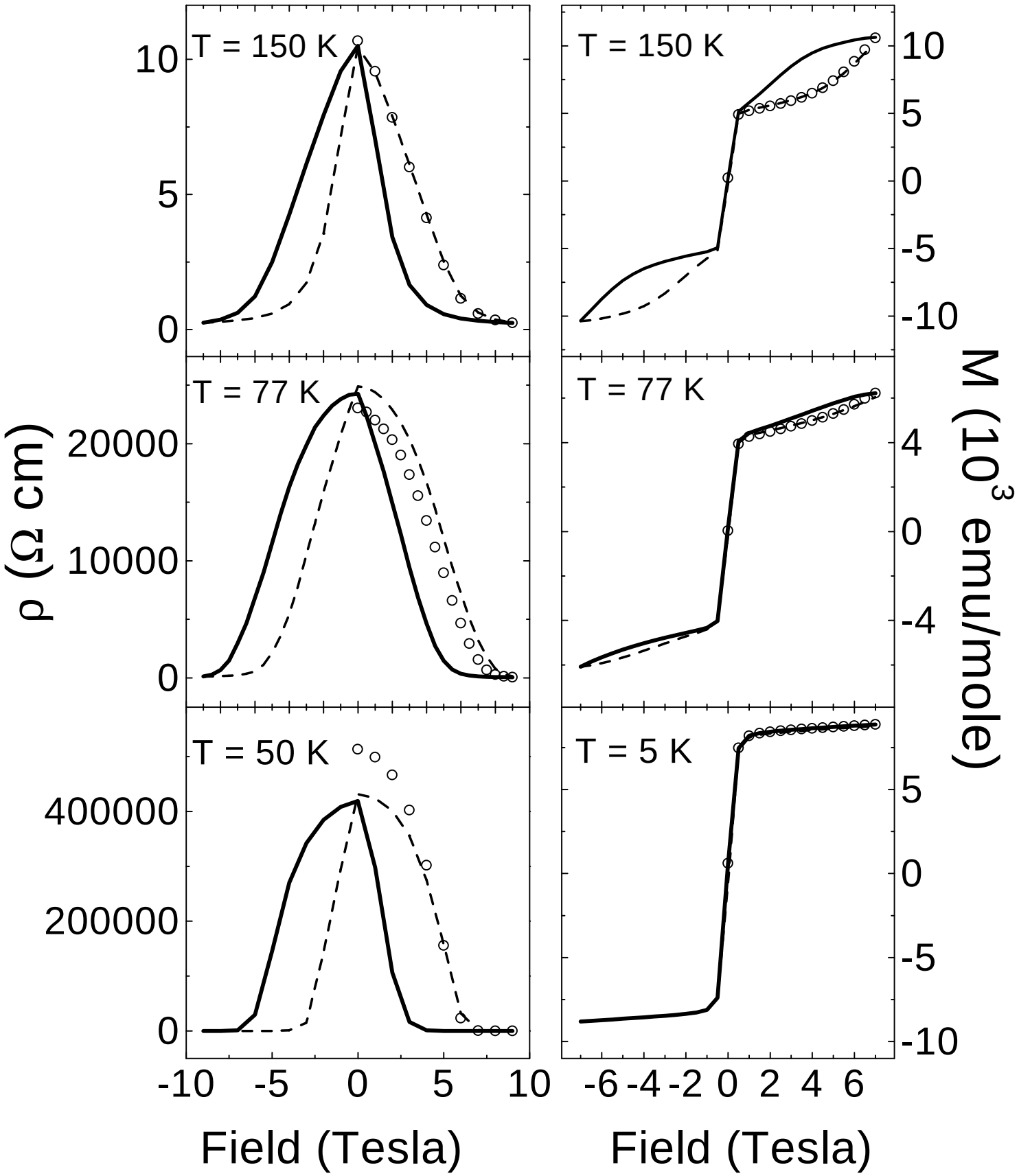

Figure 3 M. Roy *et al.*